NUCLIDE SPECIFIC ANALYSES OF ACTINIDES IN SUMP WATER USING PERALS™

Brookhaven Graphite Research Reactor SUMP TREATMENT PROJECT December 1997

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ABSTRACT

A rapid (one day) method to simultaneously determine 'total' Plutonium, Uranium, Thorium and Americium in β -contaminated environmental water samples was developed and tested at Brookhaven National Laboratory (BNL) using the PERALSTM (Photon-Electron-Rejecting-Alpha-Liquid Scintillation) system. The PERALSTM, with a 99% α -detection efficiency, can electronically filter out unwanted β/γ signals present in a sample. Water is processed using a six step procedure designed to sequentially extract 4 actinides (Pu, Am, U and Th) from a single 400 mL sample. Three commercially avialable organic-based scintillating solutions, compatible with the PERALSTM, were used to extract the 4 actinides from water. Specifically, two successive 2 mL extractions, using ALPHAEXTM, separate Pu from Am under different chemical conditions. The uranium/thorium rich aqueous fraction was then processed using two successive 4 mL amounts of THOREXTM and URAEXTM extractive scintillators which extract Th and U, respectively.

The method was first tested using individually spiked tap-waters containing α-emitting Th-230, Pu-236, Am-243 and U-232. Recoveries for each of the 4 added tracers were >95% under pre-defined chemical conditions. The Minimum Detectable Level (MDL) for a 400 mL sample counted 30 minutes in a PERALS spectrometer was < 1 pCi/L, based on separate 'method blank' measurements. Actual BNL sump water samples were collected in 400 mL glass bottles from the decommissioned Brookhaven Graphite Research Reactor (BGRR). The samples were filtered, acidified and spiked with about 100 dpm each of Th-230, Pu-236, Am-243 and U-232 yield- tracers and processed using the tested BNL method.

Because the PERALSTM cannot resolve α energies < 250 keV, some isotopes of uranium, Pu or thorium could not be individually quantified. The algorithm used to determine total Pu, Th and U activites in each extracted fraction was to integrate the total number of counts (cpm) aquired under the combined 'tracer + actinide-of interest peaks'. This count-rate was assumed to be representative of the total number of disintegrations per minute (dpm) in the spiked sample because the PERALS α -detection effciency is > 99%. For each counted fraction, the amount of spike added to the original sample (dpm), multiplied by the method recovery, was subracted from the measured total activity, yielding the net 'total' activity of the actinide-of-interest. Method recoveries for each of the 4 actinides were determined from a separate spiked tap-water sample. Data with 2σ uncertainties are presented for 6 BNL/BGRR water samples measured for total U (i.e., U-234,U-235,U-238), total Pu (i.e., Pu-238, Pu-239/240), total Th (Th-224, Th228) and Am using the PERALS method.

Plan for Sequential Extraction of Ra-226 and Actinides <u>from BGRR Sump Water</u>

Alpha specific nuclide analyses, performed by EPI/GEL Laboratory, Charleston SC in October 1997, indicated that 3 actinides (²⁴¹Am, ^{238,239,240}Pu, ^{234,235,238}U) as well as ²²⁶Ra, were present in the BGRR sump water with maximum concentrations less than 200 pCi/L (see below)

Both tri-valent actinides ²⁴⁴Cm and ²³⁷Np were not found in the BGRR sump water (which simplifies the sequential extraction scheme)

The levels of 90Sr/Y and 137Cs were 10.9 uCi/L and 4.35 uCi/L, respectively.

The presence of beta-emitting ⁹⁰Sr/Y and beta/gamma emitting ¹³⁷Cs in the BGRR water poses no problem because the PERALS can reject the unwanted signals from these radionuclides that may co-extract into the extractive scintillators.

Radionuclides in BNL/BGRR Sump Water

Nuclide	Concentration (pCi/L) 9/18/97	Concentration (pCi/L) 10/3/97
Am-241	30.2 ± 15.2	24.5 ± 3.3
Pu- 239/40 Pu-238	44.2 ± 14.1 22.4 ± 12.2	164.0 ± 21.6 4.6 ± 1.7
U-235 U-234 U-238	11.0 ± 7.2 47.0 ± 15.6 56.8 ± 16.5	14.3 <u>+</u> 2.6 69.1 <u>+</u> 8.1 72.4 <u>+</u> 8.4
Ra-226	27.5 ± 20.7	ND
Sr-90 Y-90	10,900,000 ± ?	ND
Cs-137	4,354,000 ± 62,700	ND
Tc-99	14,600 ± 1,860	ND
Н3	41,600 ± 18,900	ND

Analyses performed by EPI/GEL using HASL-300 or equivalent methods.

METHOD

A sequential extraction scheme was proposed and tested at BNL on matrix-free water samples that were spiked with 50-100 dpm amounts of:

These NIST (National Institute of Standards Tehnology) traceable radionuclides were obtained from Dr. Isabel Fisenne of the Environmental Measurements Laboratory (EML) and were later used as yield determinants when performing actual analyses on BNL's BGRR sump water samples known to contain ²⁴¹Am, ^{238,239,240}Pu, ^{234,235,238}U.

The EML tracers that were used as yield determinants (i.e., Th-230, Pu-236, U-232, Am-243) were chosen because their alpha energies were significantly different than those of the nuclides of interest (See Alpha Energy Table).

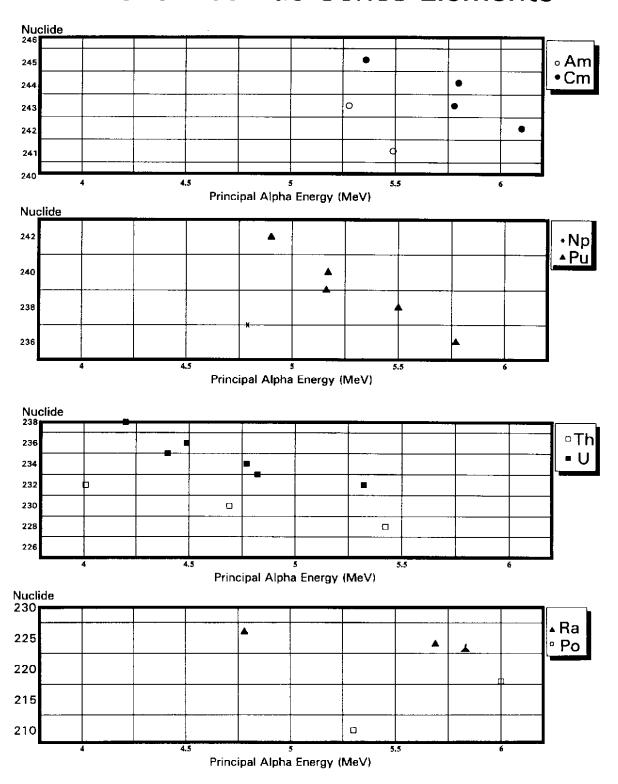
The PERALS has the capability of resolving alpha peak energies that are separated by at least 0.250 Mev; LSC cannot. Uranium 233,234,235,236 cannot be resolved by PERALS.

However, as can be seen from the Alpha Energy Table, the difference between a nuclide of interest and it's "yield tracer" alpha energy are sufficiently different (except for Am-213 and 243).

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Figure 1

Principal Alpha Energies for Radium and Actinide Series Elements



Extraction Efficiencies of Ra, U, Th, Pu, Am, Cm, and Np

in 3 Commercially Available Extractive Scintillators

by PERALS Spectrometry

Dr. Sal Scarpitta
U.S. Department of Energy
Environmental Measurements Lab
New York, NY 10014

RADIOCHEMISTRY LABORATORY WASTE MANAGEMENT WORKSHOP

41st BIOASSAY CONFERENCE November 13, 1995 Boston, MA From McDowell, J.K. and McDowell, B.L., Liquid Scintillation Alpha Spectromettry, CRC Press, Boca Raton, FL, 1994. **ETRAC** is East Tennessee Radiometric and Analytical Chemicals, Inc.

Summary of ETRAC Extractive Scintillators

(Toluene Based with Napthalene and PBBO)

	Extractant	Structure	Recommended Conditions
THOREX	Branch Primary Amine	R —N H	SO4; pH 1
URAEX	Tertiary Amine	R -N R	SO4; pH 1
ALPHAEX	НДЕНР	O C ₂ H ₅ HO -P -O -CH ₂ CH OH C ₄ H ₉	NO3; pH 2-3

HDEHP = bis-2-ethyl-hexyl phosphoric acid PBBO = 2-(4'-biphenyl)-6-phenyl benzoxazole

Tracers

Ac	Th	Pa	U	Np	Pu	Am	Cm
AW	230	Х	232	237	242	243	244
MeV	4.7	Beta	5.3	4.8	4.9	5.3	5.8

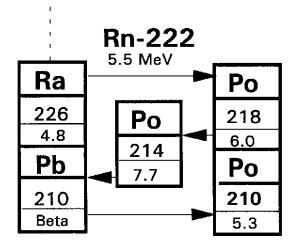


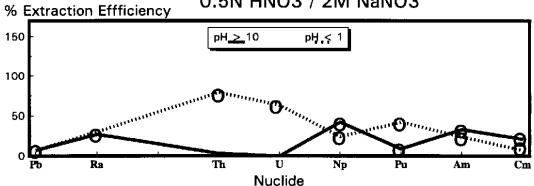
Figure 4

Extraction Efficiencies for Ra, Pb and Actinides At Extreme pH's

(1 Sigma Counting Error = 2-4%)

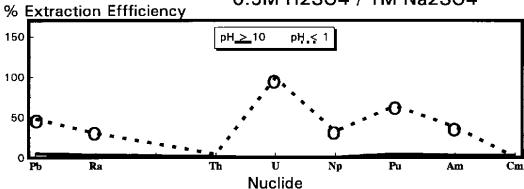
ALPHAEX

0.5N HNO3 / 2M NaNO3



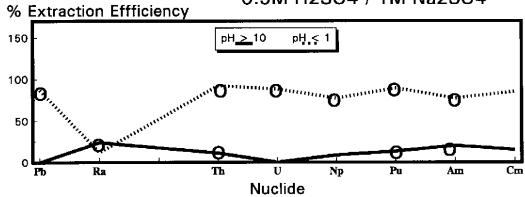
URAEX

0.5M H2SO4 / 1M Na2SO4



THOREX

0.5M H2SO4 / 1M Na2SO4



The BNL Sequential Extraction Scheme

Based on the work of Scarpitta (1995) and Dacheux (1997), an extraction scheme was devised (and tested) to sequentially extract Pu, Am, Th, U from a single 400 mL aqueous sample using each of 4 ETRACTM extractive scintillators by varying the conditions of pH and/or acid concentration.

The six step sequential extraction procedure is outlined in Figure 2 and is as follows:

- a). Add 50 100 dpm of each yield determinant tracer to a Filtered Sample Pu(IV), Th(IV), U(VI), Am(III).
- b). Reduce Pu(IV) to Pu(III) using 1 g/L Ascorbic acid.

Keeping Pu in the (III) oxidation state will <u>not</u> allow it to extract into the organic phase of the next step.

c). Acidify the solution to 0.7N with con. HNO₃. Adjust pH to 1.0 and add 2 mL of ALPHAEX and NaNO₃ salt.

The Thorium and Uranuim will extract into the **organic** phase leaving Pu(III) and Am(III) in the **aqueous** phase.

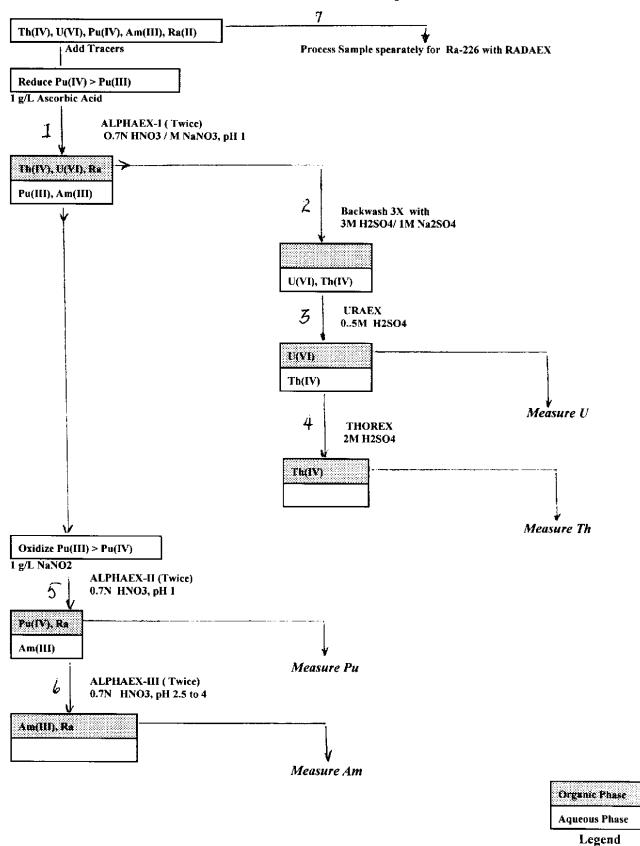
(d) The **aqueous** phase is treated separately to separate Pu from Am (See Fig. 2, Steps 5 and 6).

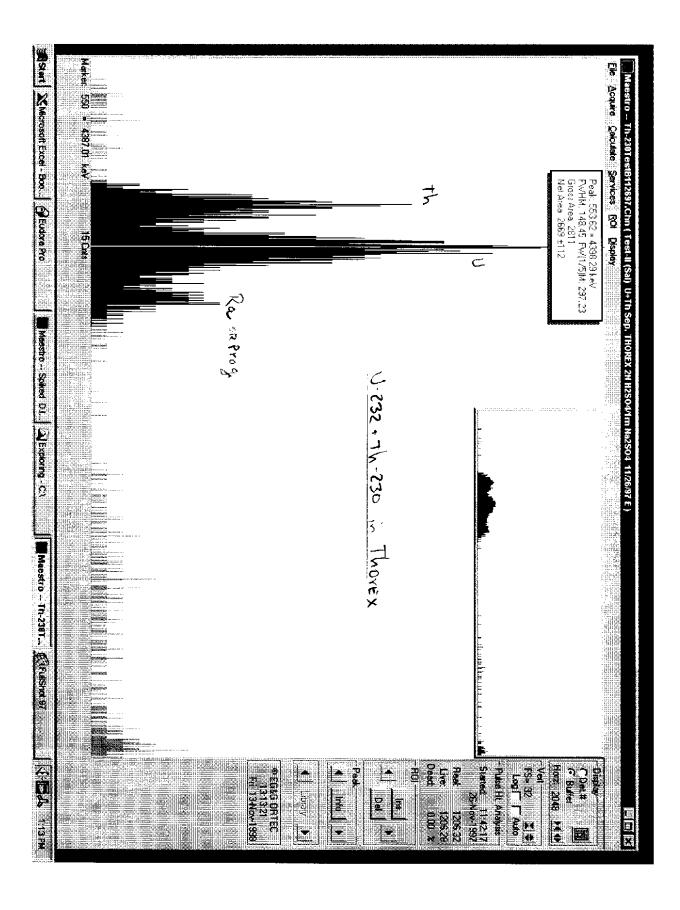
At this point, the **organic** phase is treated separately to sequentially extract both Thorium and Uranium as shown in Fig. 2, Steps 3 and 4.

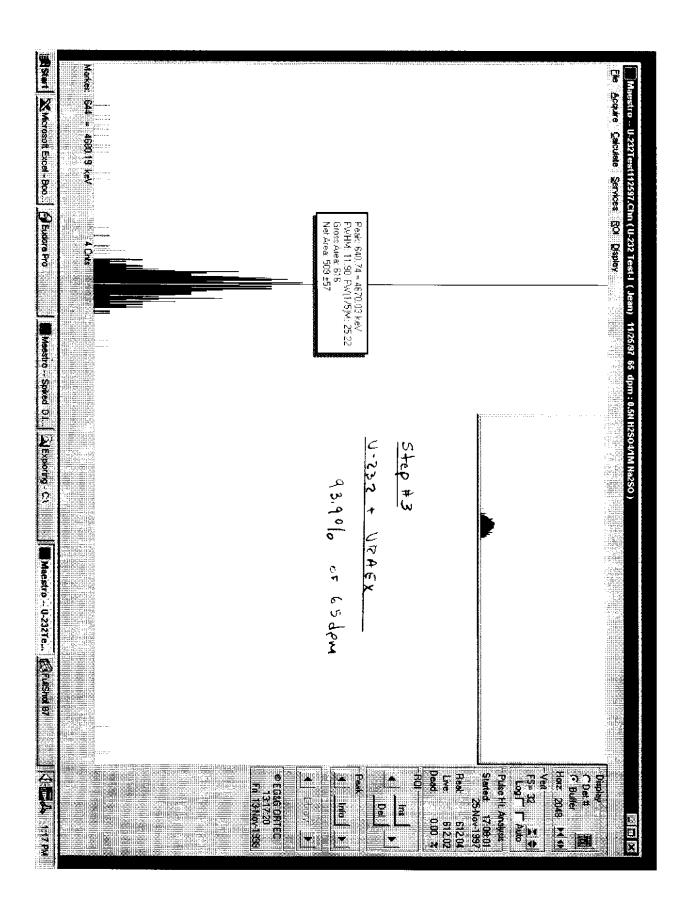
Scarpitta, S.C. and N. Krikorian. Extraction Efficiencies of Ra, Pb, U, Th, Pu, Am, Cm and Np in Five Commercially Available Extractive Scintillators Using PERALSTM, Proceedings of the 41st Annual Conference of Bioassay, Environmental and Analytical Radiochemistry, Boston, 1995.

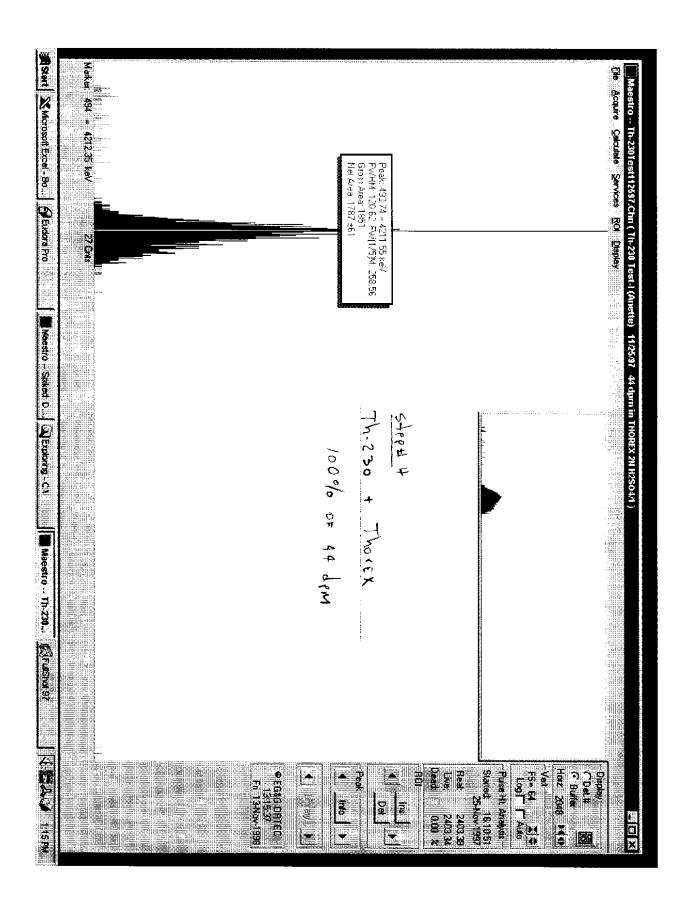
Dacheux, N and J. Auipas. Determination of Uranium, Thorium, Plutonium, Americium and Curium Ultratraces by PERALS. Anal. Chem. 69:2275-2282;1997.

Figure 2: Sequential BNL Actinide Separation Scheme









Test of Sequential BNL Separation (Refer to Fig. 2)

Test #	BNL Sep'n Step	Nuclide and dpm Added	PERLAS dpm observed	% Yield
Test I.1 (Jean) 11/25/97	3 URAEX	U-232 + Progeny 65 dpm	Single Peak 61.0	93.9%
Test I.2 (Anette) 11/25/97	4 THOREX	Th-230 (No Prog) 44 dpm	46.5	100%
Test II Sal/Jean 11/26/97	3,4 URAEX and THOREX	Mix of 61 dpm U-232 58 dpm Th-230	56.8 (U-232) 140.5 (Th-230 + Th-228)	93.1%
Test III (Pu)	ALPHAEX	41 dpm		
III.1 Pu(IV)	1,Ascor	Pu(IV)236	30.3	748
III.2 Pu(III)	5,NaNO2	Pu(III)236	5.4	13%
III.3 Pu(IV)		Pu(IV)236	24.4	60%

Calculation of Results, Uncertainties and MDL

The general equation to calculate the activity concentration (pCi/L) of a nuclide, using the PERALS combined with solvent extraction techniques is:

$$\mathbf{A_{i}} \ (\mathbf{pCi/L}) = [\underline{CR_{i} \times V_{OT} \times 1000}] + [\underline{CR_{i}}] \times V_{aq}$$

$$V_{oc} \times V_{s} \times Y_{i} V_{oc} V_{s} \times D_{i}$$

$$(1)$$

where,

 $A_i = Activity of nuclide, pCi/L$

 C_i = Net count-rate for nuclide, i, of interest (cpm)

1000 = multiplication factor to convert mL to L

D_i = Distribution coefficient of nuclide, i

 V_{aa} = Volume of aqueous phase, mL

 V_{OT} = Volume of total extractive scintillator used, mL

V_{OC} = Volume of extractive scintillator counted, mL

V_s = Volume of Original Sample, mL

Y_j = Yield factor for tracer used (unitless).

In most cases $D_i > 1000$ so that the amount of radionuclide remaining in the aqueosus phase is negligible. Equation 1 then reduces to:

$$\mathbf{A_{i}} (\mathbf{pCi/L}) = \left[\underbrace{C_{i} \times V_{OT} \times 1000}_{2.22 \times V_{oc} \times V_{s} \times Y_{I}} \right]$$
(2)

The yield (Recovery), Y_J, is determined from:

$$Y_{J} = \left[\underbrace{C_{i} \times V_{OT} \times 1000}_{c} \right]$$

$$V_{oc} \times V_{s} \times T_{a}$$

$$(3)$$

where $T_a = Activity$ of added tracer, dpm and $C_J = count$ -rate of tracer

The uncertainty, U(pCi/L) in the reported value is:

$$\mathbf{U}_{i} (\mathbf{pCi/L}) = \left[\begin{array}{c} \underline{\mathbf{V}}_{\text{OT}} \times 1000 \\ 2.22 \times \mathbf{V}_{\text{oc}} \times \mathbf{V}_{\text{s}} \times \mathbf{Y}_{\text{I}} \end{array} \right] \times \left[\mathbf{s}^{2}_{\text{G}} + \mathbf{s}^{2}_{\text{B}} \right]^{1/2}$$
(4)

where,

 s_G = standard deviation of the gross count rate, cpm

 s_B = standard deviation of the background count rate, cpm

The MDL is estimated from the following equation:

MDL (pCi/L) =
$$[2.71 + 4.65 \text{ s}_{B}] \times 1000 \text{ V}_{OT}$$
 (5)
2.22 x V_{oc} x V_s x T x Y₁

where,

T = counting time of the sample, min

 s_B = standard deviation of the background count rate (cpm) when counted for T minutes

Example of MDL

Assuming a single extraction, a count-time of 30 min, a PERALS alphabackground of 0.01 cpm,

then an MDL (see Eq. 5) of 0.2 pCi/L can be achieved when:

$$V_{OT}/V_{OC} = 2/1.5 = 1.33$$

$$V_s = 500 \text{ mL and}$$

 $Y_t = 0.99$

ALPHA STECTROSCOPY

PERALS by

Sample I.D.:		Volume (mL):	400	ı	PT:		ı
	Total Values	Taral Values				T	
	Store and a	Supple to the contract of the	•	Coder	COURTS	10101	
	Organic Used	Organic Counted	Gross	Time	per Minute	Activity	Net Tracer Net Sample
Actinide	(mL)	(mL)	Counts	(sec)	(cpm)	(dpm)	(dpm)
Ra - 226							
Pu - 238; 239 / 240	4	2					72
6m = 241	7	2					1
		ſ					1 ' '
U - 284; 285; 288	G	2		-			63
Th - 232; 228	σı	2					116
Spiked Blank		Volume (mL):	400		pH:		
	4 2 4 5 7						
	Total Volume	Total Valume		Count	Counts	Total	
	Organic Used	Organic Counted	Gross	Time	per Minute	Activity	Net Tracer Net Sample
Actinide	(mŁ)	(mL)	Counts	(sec)	(cpm)	(dpm)	(dpm)
Ra - 226							0
Pu - 238; 239 / 240	4	2					72
Am - 241	4	2					77
U - 254; 235; 236	ū	2			_		63
Th - 232; 220	Ui	2					225

1 pCi = 2.22 dpm

Sample Propurer

Sampic Knalyst

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Data Reviewer

PERALSTM DATA SUMMARY - I

Gross-Alpha (Ra + Actinide) Results of BGRR Sump-Water

A. Gross-Alpha Results (Samples were Not spiked with yield tracers)

ASL Sample ID	Analysis Date	Gross Alpha Result(*) (pCi/L)	ט
C97-12-10-09/01 (First Sample)	12/2/97	$Th(IV)+Ra(II)+U(VI)+Pu(IV) = 238$ $Pu(III) = NA$ $\Sigma = 238 \text{ pCi/L}$	± 10% ± 10%
C97-12-02-11/02 (Neutron Alarm)	12/2/97	$Th(IV) + Ra(II) + U(VI) + Pu(IV) = 172$ $Pu(III) = 90$ $\Sigma = 262 \text{ pCi/L}$	± 10% ± 10% ± 10%
Spiked Blank(#)	12/2/97	Composite Yield = 86.5% Using Th230 + U232 + Pu236	+ 3%

^{*}Samples Analyzed using ALPHAEX without Added Tracer. The reported Results were adjusted by the yield recovery of the Spiked Blank sample.

#Pu-236, Th-230 and U-232 Tracers added to D.I. water and processed separately for Yield and QA purposes. Pu(III) was determined by re-extracting aqueous sample using ALPHAEX under different chemical conditions NA means Not Analyzed. U is the estimated Uncertainty in reported result.

B. Gross-Alpha Results: Glass vs Plastic Bottles (L-Dups)

ASL Sample ID	Analysis Date	Gross Alpha Result(*) (pCi/L)	U
C97-12-03-16/01P	12/3/97	$Th(IV)+Ra(II)+U(VI)+Pu(IV) = 93$ $Pu(III) = 23$ $\Sigma = 116 \text{ pCi/L}$	± 10% ± 10% ± 10%
C97-12-03-16/01G	12/3/97	$Th(IV)+Ra(II)+U(VI)+Pu(IV) = 83$ $Pu(III) = 18$ $\Sigma = 101 \text{ pCi/L}$	± 10% ± 10% ± 10%
Spiked Blank (#)	12/4/97	Composite Yield = 87.7% Using Th230 + U232 + Pu236	<u>+</u> 3%

^{*}BGRR Samples Analyzed using ALPHAEX without Added Tracer. The reported Results were adjusted by the yield recovery of the Spiked-Blank sample.

[#]Pu-236, Th-230 and U-232 Tracers added to D.I. water and processed separately for Yield and QA purposes. Pu(III) was determined by re-extracting aqueous sample with ALPHAEX under different chemical conditions. U is the estimated Uncertainty in reported result.

PERALSTM DATA SUMMARY - II

Nuclide-Specific Actinide Results of BGRR Sump-Water (All Samples Spiked with 100 dpm each of Pu-236, Am-243, U-232 and Th-230)

A. Base-Line Sump Sample (Beginning of Pumping)

ASL Sample ID	Analysis Date	Result (pCi/L)	Uncertainty
C97-12-02-08/02	12/8/97	$Pu_{Tot} = 140$	<u>+</u> 25%
	D	Am/Ra = 126	<u>+</u> 25%
et .	U	$U_{Tot} = 3$	<u>+</u> 25%
11	D	$Th_{Tot} = 5$	<u>+ 25 %</u>
R	D.	$\Sigma = 274$	+ 25%

B. Neutron-Alarm Sump Sample (Pumping Stopped)

ASL Sample ID	Analysis Date	Result (pCi/L)	Uncertainty
C97-12-02-11/01	12/8/97	$Pu_{Tot} = 160$	<u>+</u> 25%
11	n	Am/Ra = 84	<u>+</u> 25%
"	94	$U_{Tot} = 6$	<u>+ 25</u> %
11	n	$Th_{Tot} = 33$	± 25%
11	01	$\Sigma = 283$	<u>+</u> 25%

C. Restart of Pumping Sump Sample

ASL Sample ID	Analysis Date	Result (pCi/L)	Uncertainty
C97-12-10-09/01	12/11/97	Pu _{Tot} = 164	± 25%
tı .	"	Am/Ra = <2*	+ 25%
	**	$U_{Tet} = 48$	± 25%
7	u	$Th_{Tot} = 26$	± 25%
	н	$\Sigma = 238$	<u>+</u> 25%

^(*) means Am was not effectively extracted and result was MDL.

D. Spiked D.I. Blank

Sample ID	Analysis Date	% Recovery of Added Tracer	MDL (pCi/L)
Spiked Blank	12/12/97	Pu-236 = 88.3 ± 3%	2.0
H	11	$Am-243 = 96.7 \pm 3\%$	2.0
11	11	U-232 = 92.4 <u>+</u> 3%	3.0
PF .	tr	Th-230 = 82.0 + 3%	3,0

Tracers added to D.I. water and processed separately for QA and Yield purposes.

MDLs for U and Th are 3.0 because of larger volume of extractive scintillator used.

Dr. Scarpitta was for 4 years one of the 2 coordinators of the U.S. DOE's Environmental Measurements Lab (EML) Quality Assessment Program (QAP) while he was Supervisor of the Radioanalytical Chemistry Division in 1991-1995. Besides 15 other publications, he is the principal author of 2 recent studies performed and published while at EML, New York. They are: (a) "Calibration of a Liquid Scintillation Counter for Alpha, Beta and Cerenkov Counting", Report EML-583, July, 1996 and (b) "Cerenkov Counting as a Complement to Liquid Scintillation Counting", Appl. Radiat. Iso. 47(8):795-800:1996. He first presented his work with the PERALS spectrometer at the 41st Annual Conference of Bioassay, Environmnetal and Radioanalytical Chemistry in Boston (1995). For the past 2 years he has been a full-time member of the

Environmental Safety and Health Division and head of the BNL Analytical Services Lab.